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Extraction Study On The Colour Reaction For Cobalt (II) With The 2-Hydroxy-5-Nitrothiophenol - Di-, Triphenylamine - Water - Chloroform System

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***Abstract*—The conditions for the complexation of cobalt (II) with HNTPh and Am (DPhA and TPhA) are optimized, such as the formation of the complex in time (300 minutes), pH of the medium (pH_{op} 3.6-5.2), the excess of the reagent, and the conditions for obeying the Bouguer-Lambert-Beer law(0.06-20 µg / 5 ml). The spectral characteristics of the complex (λ= 560-565 nm) and the HNTPh reagent (λ= 295 nm) were studied which showed high sensitivity and contrast (λ= 265-270 nm) and the true molar coefficient ($\varepsilon = (3.4\text{-}3.6) \times 10^4$) of light absorption was determined. The mole ratio of cobalt: agent is determined by two methods; the equilibrium shift method and the Asmus straight line method, and in both cases the Co: HNTPh: Am = 1: 2: 2 composition. The interval of obedience to the Bouguer-Lambert-Beer law (0.06-20 µg / 5 ml) and the Sendel sensitivity of 0.0111 - 0.0175 µg / cm^2 are shown. Based on the achieved results and revealed regularities, a photometric technique for determining cobalt (II) with HNTPh and Am. The selectivity of the developed methodology was studied. The developed technique is applied to the analysis of various objects, the results obtained are processed by the method of mathematical statistics.**

***Keywords*—Cobalt, 2-hydroxy-5-nitrothiophenol, hydrophobic amines, diphenylamine, triphenylamine, chloroform.**

1. Introduction

The urgency of the development of simple, rapid and sensitive techniques for determining cobalt is due to the extensive use of this metal in industry, on the one hand, and its toxicity on the other [1]. Despite the development of atomic-spectral methods for determining cobalt, the extraction-photometric method, which does not require an expensive equipment, is simple in execution and is available for small production and agrochemical laboratory.

In connection with these circumstances, it is very attractive to extract cobalt

in the form of thiocyanate complexes, which have a characteristic absorption spectrum and are well extracted from the aqueous phase by various extractants [2]. Although the thiocyanate method for determining cobalt is known more than a hundred years and finds so wide practical application that it stands out as an independent direction in the analytical chemistry of cobalt [3], its capabilities are constantly expanding by using new extractants.

As a reagent for cobalt, a number of reagents belonging to the class of o, o-hydroxyaminazo compounds are proposed [4]. For cobalt complexes with them, the conventional molar light absorption coefficients are calculated. They are 4.37 × 10^4 for nitrazone F, 3.75 × 10^4 for chloroxaminase F. The ratio of complexes is studied by saturation, isomolar series and Asmus, it is 1: 1 and 1: 3. It has been established that alkali and alkaline-earth metals, W^{4+}, Mo^{4+}, Mn^{2+}, Pb^{2+}, V^{5+}, Cr^{3+}, and others practically do not interfere with the determination of cobalt with nitrosan. Al^{3+} and Cd^{2+} interfere in large quantities due to hydrolysis. In their presence, the determination is carried out at pH> 10.0. Under optimal conditions of complexation, Zn^{2+}, Cu^{2+} and Fe^{3+} strongly interfere.

A spectrophotometric method for determining trace amounts of cobalt, nickel, and copper ions was developed [5] after the adsorption of their 2-aminocyclopentene-2-dithiocarboxylate complexes on microcrystalline naphthalene. These complexes are adsorbed on microcrystalline naphthalene at pH = 4.5 after shaking for 5 minutes. The resulting solid mass is separated by filtration and is dissolved in dimethylformamide. For the analysis of the three-component mixture Co^{2+}, Ni^{2+}, Cu^{2+}, the absorption spectra were processed using a calibration multiparameter method of partial least squares. The detection limits for Co^{2+}, Ni^{2+} and Cu^{2+} were 3.3; 10.0 and 0.8 µg / ml. The proposed method has also been successfully applied to determine the content of Co^{2+}, Ni^{2+} and Cu^{2+} in alloys.

Sorption of Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} sorbent POLIORGS was studied [6] and concentrating conditions were chosen for the analysis of small volumes of natural waters. The behavior of these metals has been studied and the atomic absorption regimes have been established in the aqueous suspension of the sorbent. A sorption-atom-absorption method for determining Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} in seawater has been developed. The limits of detection of elements are 0.4 $\mu g L^{-1}$ for Cu^{2+} and Ni^{2+}, 0.05 μgL^{-1} for Co^{2+}, 0.2 μg L^{-1} for Pb^{2+} and 0.1 μg L^{-1} for Cd^{2+}.

The authors of Ref. [7] found the optimum conditions for the concentration of Ni^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+} on silica by C-120 siloxane modified with 4- (2-tialylazo) resorcinol, and the colorimetric characteristics of the complexes were determined. It is shown that the separation criterion is satisfied by complexes of nickel and zinc. A colorimetric method for the separate determination of 0.05-1.00 μg L^{-1} was developed of nickel and 0.15-5.0 μg mL^{-1} of zinc.

A technique was developed [8] for the spectrophotometric determination of the Co^{2+}, Ni^{2+}, Cu^{2+}, Pd^{2+}, Ru^{2+} and Mo^{6+} macroquantities after extraction of their isoamylxanthogenates with molten naphthalene. The optimum condition for determining Co^{2+} at pH 3.0-8.0 is selected, the complex is formed by the ratio 1: 2; The molar coefficient of light absorption is equal to 2.06×10^4 at 360 nm, the Sendel sensitivity is 0.0052 μg cm^3, Sr = 0.0081.

The possibility of direct determination of Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} and Ni^{2+} in concentrated solutions of calcium chloride by the method of electrothermal atomic absorption spectrometry was shown in [9]. As chemical modifiers, ascorbic and oxalic acids, as well as magnesium nitrate, have been studied. The best modifier was oxalic acid. Despite the use of an atomic absorption spectrometer with a relatively ineffective background correction system (with a deuterium lamp) in the presence of oxalic acid, it is possible to confidently determine the studied elements to a concentration of calcium chloride in a solution of 6%. Due to the fact that cadmium evaporates before the main part of this matrix, it can be determined without a modifier.

The method [10] of the sorption concentration of Fe^{3+}, Co^{2+}, Pb^{2+}, Cd^{2+} and Cr^{3+} was developed on a column with an Ambersorb 563 sorbent from the sample solution and the eluent was set by a peristaltic pump. In NH_3-NH_4Cl buffer solution (pH = 9.0), these ions were quantitatively retained by the sorbent. Then they were eluted with 5 ml of 0.25 M HNO_3 at a rate of 5 ml min^{-1}. The detection limits of Cd^{2+} and Pb^{2+} are 0.33 and 72 μg L^{-1}, respectively. The relative standard deviation is less than 0.10. The method is used to determine the ions Fe^{3+}, Co^{2+}, Pb^{2+}, Cd^{2}+ and Cr^{3+} in drinking and sea water samples (recovery> 95%).

The optimum conditions for the complexation of cobalt with nitroso-P-salt (HPC) in the presence and absence of ascorbic acid were found in [11]. The molar coefficients of the colorimetric functions of the complexes were calculated and it was shown that only the colorimetric functions make it possible to distinguish the complexes of cobalt (II) and cobalt (III), while the optical characteristics are practically identical. For practical purposes, it is better not to inject ascorbic acid and obtain a kinetically inert cobalt (III) complex with a nitroso-P salt. Under optimum complexation conditions, the maximum light absorption of the reagent is at 360-380 nm from the obtained data [12], 430, 490 and 710 nm are chosen as the characteristic wavelengths. At 710 nm, only the iron (III) complex with HPS is absorbed to the maximum and a potential for separate determination of cobalt and iron appears in a joint presence by the method of two-wave spectrophotometry.

Oxyphenolate and hydroxthiophenolate complexes of cobaltare insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [13-14]. In this respect, a very promising reagent is hydroxthiophenols, which contains one hydroxyl and one sulphohydryl groups and is a sulfur-containing analogue of mononuclear poly-phenols with one oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of Cobalt (II) with hydroxthiophenols in the presence of hydrophobic amines (Am). From hydroxthiophenol 2-hydroxy-5-nitrothiophenol (HNTPh) were used in the presence of hydrophobic amines (Am). As hydrophobic amine diphenylamine (DPhA) and triphenylamine (TPhA) were used.

2. Experimental

2.1. Reagents and Apparatus

Cobalt standard solution (1000 mgL^{-1}; $Co(NO_3)_2$) was purchased from Merck Darmstadt (Germany). Working solutions (C_{Co} = 1.7×10^{-5} mol L^{-1}) were prepared by diluting appropriate volumes of the stock solution. The concentration of the cobalt solution was adjusted gravimetrically [15].

HNTPh were synthesized according to the procedure [16]. The purity was checked by determining the melting point and chromatography on paper. The HNTPh was identified by IR and NMR spectroscopy: IR (KBr): [3462 см$^{-1}$ ν(OH), 2564 см$^{-1}$ ν(SH), 3045 см$^{-1}$ ν(CH), 1700 см$^{-1}$ ν(NO_2), 1535 см$^{-1}$ ν(C_6H_5)]; 1H NMR (300,18 MHs, C_6D_6); [δ 5.16 (s, 1H-OH), δ 3.25(s, 1H - SH), δ 7.18 (s, 2H Ar-H), δ 7.41 (s, 1H - Ar-H)].

0.01M solutions of HNTPh and Am in chloroform were used in the work. The HNTPh was purified by reprecipitation from ethanol solutions by addition of water and then by distillation.

To create the necessary pH, fixated HCl (pH 0-3) and CH_3COOH + CH_3COONH_4 buffer solutions (pH 4-12) were used. The ionic strength of the solutions was kept constant (μ = 0.1) by introducing the calculated amount of 1M KNO_3.

The optical density of the solutions was measured on a SF-26 spectrophotometer and on a KFK-2 photoelectric colorimeter in a cuvette with a layer thickness of ℓ = 1 cm and 0.5 cm, respectively. The pH of the solutions was monitored with an I-120 ionomer with a glass electrode. IR spectra were recorded on a UR-20 spectrophotometer in the 400-4000 cm^{-1} region. All of these devices were tested by the state.

2.2 General Procedure

2.2.1 General Procedure for the Determination of Cobalt (II)

Portions of stock solutions of Cobalt (II) varying from 0.1 to 1.0 mL with a 0.1 mL step, a 2.2 – 2.5 mL portion of a 0.01 M solution of HNTPh, and a 2.5 – 3.0 mL portion of a 0.01M solution of Am were placed in to calibrated test tubes with groundglass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding CH_3COOH + CH_3COONH_4 buffer solutions (pH 4-12). The volume of the aqueous phase was increased to 20 mL using distilled water. In 8 - 10 minnute after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 540 nm (ℓ=0.5cm).

2.2.2. Determination of Cobalt in metallic nickel

A sample weighing (8 g) is dissolved in 30 ml of a mixture (3: 1) of HCl and HNO_3. The solution is evaporated to a syrupy state, the salts are dissolved in water and the solution is transferred to a volumetric flask. 25 ml. An aliquot (10 ml) was taken, a certain amount of cobalt (30 μg) was added thereto and cobalt with HNTPh and Am was extracted and photometrically determined under optimal conditions.

2.2.2. Determination of Cobalt (II) in Steel

A weighed sample of 0.2 g was dissolved in 20 ml of H_2SO_4 (1: 1) was oxidized with a few drops of concentrated nitric acid and evaporated twice lo vapor SO_3. The precipitated salt was dissolved in 20 ml of 15% tartaric acid under heating, the solution was cooled, adjusted with water to 100 ml in a volumetric flask, stirred and filtered. An aliquot of 5 ml was put into a separatory funnel, was added 1 ml of 10% hydroxylamine solution, 1 ml of 3% ascorbic acid and was determined cobalt using the proposed procedures.

2.3.3. Determination of cobalt (II) in tap water.

Pour 2 liters of water into a flask and evaporate to dryness. The dry residue is dissolved in a buffer solution of pH 4 and transferred to a 50 ml flask by filtration. In an aliquot (3 ml), photometric determination of cobalt.

3. Results and Discussion

Co (II) reacts with 2-hydroxy-5-nitrothiophenol and gives complexes that are insoluble in non-polar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P anion exchangers have demonstratedthe anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the yellow dithiophenolate complexes of Cobalt(II) moved to the cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When diphenylamine and triphenylamine were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

3.1. Selection of extractant. To extract the complexes, $CHCl_3$, CCl_4, C_6H_5Cl, C_6H_6, $C_6H_5–CH_3$, $C_6H_4(CH_3)_2$, *iso*-C_4H_9OH, C_4H_9OH, *iso-* $C_5H_{11}OH$, $C_2H_4Cl_2$ were used. The extractability of the complexes was evaluated by the distribution coefficient and the degree of extraction. The best extractants were $CHCl_3$, $C_2H_4Cl_2$ and C_6H_5Cl. All further studies were carried out with $CHCl_3$. The content of cobalt in the organic phase was determined photometrically by 2-nitroso-1-naphtol [3] after stripping, and in the aqueous phase by the difference. With a one-time extraction (R,%) by chloroform, 96.0 - 97.0% of cobalt is extracted as a MLC.

3.2. Effect of the pH of the aqueous phase. Light absorption spectra of cobalt (II) complexes with HNTPh and Am were studied in a wide range of pH of the medium. The maximum yield of complexes is observed at pH 1.4-8.2. Hence further analytical investigations were carried out in media of pH 3.6-5.2 (Fig. 1). Extraction of Co(II) enhanced with the increase in the acidity of the initial solution. The further increase in acidity lead to the gradual decrase of recovery, which was obviously associated with a decrease in the concentration of the ionized form of HNTPh. pH ≥ 8.2 complexes are not practically extracted, which, apparently, is associated with a decrease in the Am protonation degree.

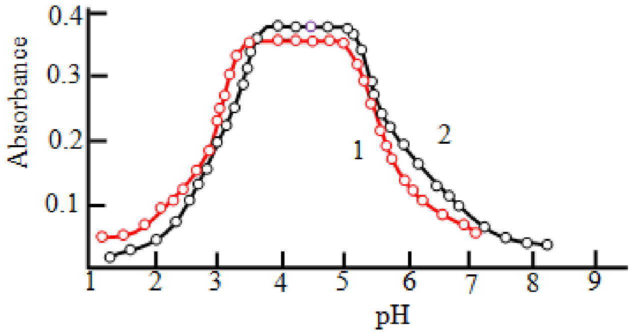


Fig. 1: Absorbance of Co- HNTPh -Am extracts function of the pH of the aqueous phase.

1. Co– HNTPh – DPhA, 2. Co– HNTPh – TPhA

$C_{Co(II)}$ = 1.7×10^{-5} M, C_{HNTPh} = (1.12-1.25)×10^{-3} M, C_{Am} = (0.90-1.30)× 10^{-3} M, λ=540 nm, KFK-2, ℓ=0.5 cm

3.3. Influence of Reagent Concentration

For the formation and extraction of MLC, a 20-25-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by (1.12-1.25)×10^{-3} M HNTPh and (0.90-1.30)× 10^{-3} M Am. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction.

3.4. A study of the stability of the optical density of the cobalt (II) complex with HNTPh and Am in time.

To determine the stability of the color of the cobalt complex in time, the optical density of the solutions was measured at definite intervals of time.

Method of work: 1.0 ml of cobalt (II) solution, (Co^{2+} = 10 μg / mL), 1.0 mL of 0.01M reagent solution, 5.0 ml of sodium acetate buffer solution were added to 25 ml volumetric flasks with a pH of 3.6-5.2 and the volume was adjusted to the mark with distilled water. The optical density of the complex was measured on KFK-2, ℓ = 0.5 cm. The results of the measurements are shown in Table 1.

Table 1: A study of the stability of the optical density of the cobalt (II) complex with HNTPh and DPhA in time.

Time minutes	3	5	10	20	30	40	50	60	80	100
A	0.180	0.285	0.340	0.340	0.340	0.340	0.340	0.340	0.340	0.340
Time minutes	140	180	200	220	240	260	300	320	340	380
A	0.340	0.340	0.340	0.340	0.340	0.340	0.340	0.288	0.250	0.170

It can be seen from the table data that the optical density of the complex does not change for 300 minutes, which is full enough to produce reproducible results.

3.5. The study of the ordering of the components of the reaction

From the experimental data obtained, it can be seen that the maximum optical density is observed at the order of the discharge of the components: cobalt (II) + HNTPh + Am + $CHCl_3$ + CH_3COOH + CH_3COONH_4 + water. In further studies, this order of draining the components was used as the optimal one.

3.6. Spectral characteristics of cobalt (II) complexes with HNTPh and Am.

The spectra of HNTPh and its complex with cobalt (II) are shown in Fig. 2. It can be seen from the figure that in the light absorption spectrum of the cobalt (II) complex there is one expressed maximum at 560-565 nm, and the maximum light absorption of the HNTPh reagent is observed in the shorter-wave region of the spectrum, at 295 nm, which characterizes the contrast between the color of the complex and the reagent, is 265-270 nm, which contributes to the sensitivity of the method.

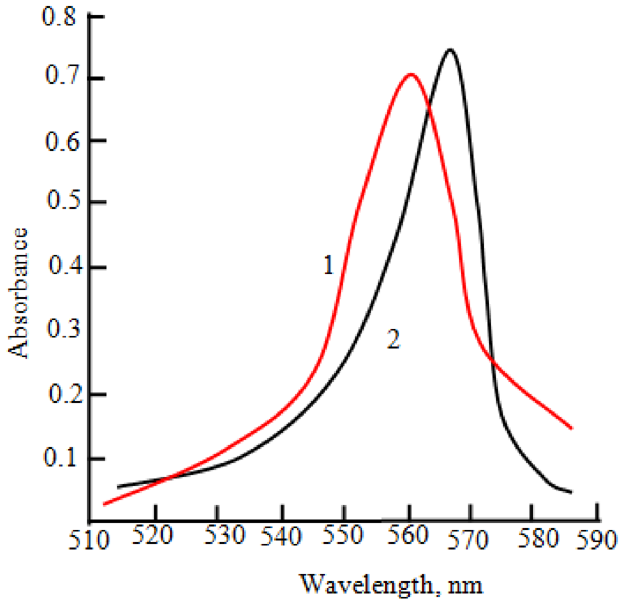


Fig. 2: Absorption of mixed-ligand complexes

1. Co– HNTPh – DPhA, 2. Co– HNTPh – TPhA

$C_{Co(II)}$ = 1.7×10^{-5} M, C_{HNTPh} = (1.12-1.25)×10^{-3} M, C_{Am} = (0.90-1.30)× 10^{-3} M, pH 3.6-5.2, SF-26, ℓ=1.0

Sensitivity of the method was calculated by the Sendel method in μg/cm² per 0.001 light absorption unit according to the formula:

$$S_s = \frac{G \times \ell \times 0.001}{A \times 25} = \frac{20.0 \times 1.0 \times 0.001}{0.34 \times 5} = 0.0175\,\mu g / cm^2$$

where *G* is the amount of cobalt, in μg; *A*-optical density.

According to the calculated value of Sendel, it can be concluded that the technique for determining cobalt (II) is quite sensitive. The molar absorptivity of the complex was calculated with Komar method [17] to be ε= (3.4-3.6)× 10^4 L mol^{-1} cm^{-1}.

3.7. Stoichiometry of the Complexes and the Mechanism of Complexation

The stoichiometric reaction coefficients were established by the methods of the Asmus straight line and the equilibrium shift [17]. The formation of MLC can be represented as follows. Cobalt ions interacting with two molecules of HNTPh form a doubly charged anionic complex, which is extracted with two molecules of protonated Am (Fig. 3).

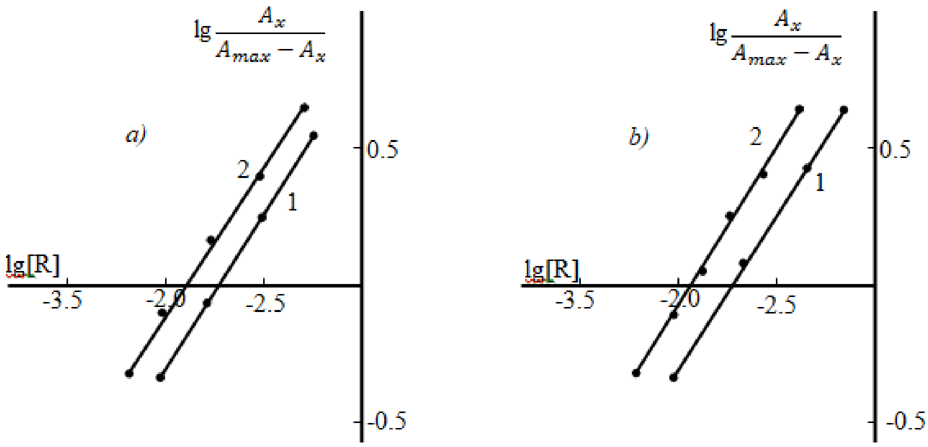


Fig.3: Determination of the ratio of components by the equilibrium shift method for (a) Co (II)- HNTPh-DPhA and (b) Co (II)- HNTPh-TPhA. 1- Co (II) : HNTPh; 2- Co (II): Am.
$C_{Co(II)} = 1.7\times10^{-5}$ M, SF-26, λ=540 nm, ℓ =1.0 cm.

The pH of the start of precipitation of $Co(OH)_2$ is 8.0, and the pH of the total precipitation is -10.0 [18]. HNTPh is a sufficiently strong reducing agent, so oxidation of Co (II) is not possible. Thus, Co(II) in the complexes is in the unhydrolyzed state. The number of protons displaced by cobalt from one HNTPh molecule turned out to be 2 [19].

The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3451 cm^{-1} observed in the spectrum of HNTPh, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2587 cm^{-1} shows that the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1385 cm^{-1} indicates the presence of a protonated diphenylamine (Fig. 4) [20].

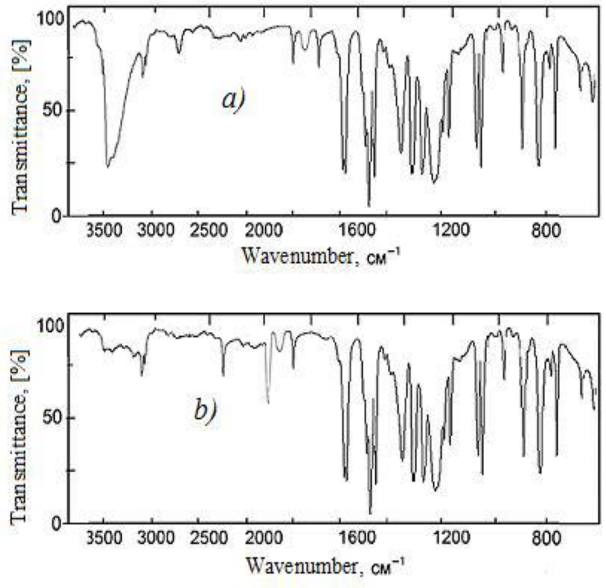
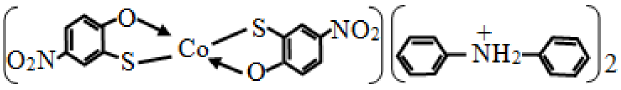


Fig. 4: IR spectrums of HNTPh (*a*) and the Co (II)- HNTPh-DPhA (*b*).

Calculation of extent of polymerization of complexes was carried out on the equation [21]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form (γ =1.06-1.10).

Proceeding from the obtained data, we propose the following stucture for the extracted ternary complex (scheme).



Scheme. Structure of complex $[Co(HNTPh)_2](DPhAH)_2$

3.8. Influence of interfering ions

To evaluate the complex applicability for photometric determination of cobalt, we examined the influence of foreign ions and reagents. The results showed that great excesses of alkali, alkali earth, and rare earth elements, as well as NO_3^-, ClO_4^-, SO_4^{2-} and CH_3COO^- do not interfere determination of cobalt with HNTPh and DPhA. Interference of most cations masked by the addition of complexone III. Tartrate mask the milligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper-thiourea. The results are summarized in Table 2.

Table 2: Effect of foreign ions on the extraction of 20 μg cobalt (II)

Foreign ions (FI)	μg	FI-to-Co ratio	Co found	R,%
Mo(VI)	5	250	19.85	97.0
W(VI)	5	250	19.88	97.7
Cr(VI)	2.5	125	19.91	98.2
Cr(III)	1.5	75	19.80	96.0
Fe(II)	0.5	2.5	19.25	85.0
Fe(III)	0.5	2.5	20.90	118.0
V(IV)	0.05	2.5	20.55	111.0
V(V)	0.05	2.5	19.25	85.0
Cd^{2+}	0.2	10	19.86	97.2
Cu^{2+}	0.06	3	20.17	103.4
Al^{3+}	5	250	20.08	101.6
Zn^{2+}	0.5	25	20.04	100.8
Zr(IV)	3.0	150	20.18	103.5
Nb(V)	0.5	2.5	19.25	85.0
Ti(IV)	2.5	125	20.17	103.4
Ni^{2+}	2.5	125	19.91	98.2

In conclusion the analytical parameters pertaining to the proposed method are given in Table 3.

Table 3: Optical characteristics, precision and accuracy of the spectrophotometric determination of Co(II) with HNTPh and Am

Parameter	$[Co(HNTPh)_2](DPhAH)_2$	$[Co(HNTPh)_2](TPhAH)_2$
The pH range of education and extraction	1.4-7.2	1.4-8.2
The pH range of maximum extraction	3.6-5.0	3.7-5.2
λ_{max} (nm)	560	565
Molar absorptivity (L $mol^{-1}cm^{-1}$)	3.4×10^4	3.6×10^4
Sandell's sensitivity (μg cm^{-2})	0.0175	0.0111
R,%	96.0	97.0
The equation of calibration curves	0.020+0.098x	0.018+0.102x
Beer's law range (μg ml^{-1})	0.06-18	0.06-20
Correlation coefficient	0.9988	0.9985

3.9. Effect of Cobalt(II) Concentration The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Co(II) may be determined in the range 0.06-20 $\mu\mu$g/ml (table 3).

Table 4 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of cobalt with the earlier known procedures [2,3, 11, 22, 23].

Table 4: Comparative characteristics of the procedures for determining of cobalt

Reagent	pH (solvent)	λ, nm	$\varepsilon\cdot 10^{-4}$	Beer's law range (μg·mL^{-1})	Ref.
2,3,5-triphenyl-2H-tetrazolium chloride	5.2-5.8	525	4.26	0.2 - 1.5	[22]
1-nitroso-2-naphtol	≥3	415	2.9		[2,3,11, 23]
2-nitroso-1-naphtol	≥4	365	3.7		[2,3, 11, 23]
Nitroso-R-salt	weakly acidic medium	415	3.5		[2,3, 23]
HNTPh - DPhA	3.6-5.0 ($CHCl_3$)	560	3.4	0.06-18	
HNTPh -TPhA	3.7-5.2 ($CHCl_3$)	565	3.6	0.06-20	

3.10. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Co(II) in various objects. The results presented in Table 5, 6 and 7 indicate the successful applicability of the proposed method to real sample analysis.

Table 5: Results of spectrophotometric determination of cobalt in metallic nickel (*n* = 6, *P* = 0.95).

Method	Found Co, % 10^{-5} $\bar{x}$	S× 10^{-5}	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Known methods				
1-nitroso-2-naphtol	7.92	0.316	0.040	(7.92±0.33)· 10^{-5}
2-nitroso-1-naphtol	7.90	0.395	0.050	(7.90±0.44) · 10^{-5}
Proposed method				
HNTPh - DPhA	7.8	0.195	0.025	(7.8±0.20) · 10^{-5}
HNTPh -TPhA	7.8	0.218	0.028	(7.8±0.23) · 10^{-5}

Table 6: Determination of Cobalt in steel (*n*=3, *P*=0.95)

Compound	*X*	Sx	*ε*	S_r	µ
Steel M 441(0.012% Co)					
Co-HNTPh-DPhA	0.0124	0.311 ×10^{-3}	0.33 ×10^{-3}	0.026	0.0124±0.00033
Co-HNTPh-TPhA	0.0123	0.267×10^{-3}	0.29×10^{-3}	0.023	0.0123±0.00029
Steel №156 (0.56% Co)					
Co-HNTPh-DPhA	0.582	0.021	0.020	0.033	0.582±0.02
Co-HNTPh-TPhA	0.573	0.022	0.024	0.038	0.573±0.024

Table 7: Results of the determination of cobalt (II) in drinking water (*n* = 6, *P* = 0.95)

Method	Found in the sample, mg / L	S	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Known methods				
1-nitroso-2-naphtol	0.0205	0.00044	0.022	0.0205±0,0005
2-nitroso-1-naphtol	0.0219	0.00040	0,018	0.0219±0,0004
Proposed method				
HNTPh - DPhA	0.0182	0.00022	0,012	0.0182±0,0002
HNTPh -TPhA	0.0179	0.00027	0,015	0.0179±0.0003

4. CONCLUSIONS

1. The conditions for the complexation of cobalt (II) with HNTPh and Am (DPhA and TPhA) are optimized, such as the formation of the complex in time, pH of the medium, the excess of the reagent, and the conditions for obeying the Bouguer-Lambert-Beer law.

2. The spectral characteristics of the complex and the HNTPh reagent were studied which showed high sensitivity and contrast (λ= 265-270 nm) and the true molar coefficient of light absorption was determined.

3. The mole ratio of cobalt: re: agent is determined by two methods; the equilibrium shift method and the Asmus straight line method, and in both cases the Co: HNTPh: Am = 1: 2: 2 composition.

4. The interval of obedience to the Bouguer-Lambert-Beer law (0.06-20 µg / 5 ml) and the Sendel sensitivity of 0.0111 - 0.0175 µg / cm^2 are shown. Based on the achieved results and revealed regularities, a photometric technique for determining cobalt (II) with HNTPh and Am.

5. The selectivity of the developed methodology was studied. The developed technique is applied to the analysis of various objects, the results obtained are processed by the method of mathematical statistics.

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